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(54) **Title:** THIN FILMS, STRUCTURES HAVING THIN FILMS, AND METHODS OF FORMING THIN FILMS

(57) **Abstract:** The invention described herein relates to new titanium-comprising materials which can be utilized for forming titanium alloy barrier layers for Cu applications. Titanium alloy sputtering targets can be reactively sputtered in a nitrogen-comprising sputtering gas atmosphere to from titanium alloy nitride film, or alternatively in a nitrogen-comprising and oxygen-comprising atmosphere to form titanium alloy oxygen nitrogen thin film. The thin films formed in accordance with the present invention can contain a non-columnar grain structure, low electrical resistivity, high chemical stability, and barrier layer properties comparable or exceeding those of TaN.

AMENDED CLAIMS

[Received by the International Bureau on 12 June 2003 (12.06.03):
Claims unchanged: 8-14, 18, 19; amended: 7, 17, 20; cancelled: 1-6, 15, 16 (4 pages)]

The invention claimed is:

1. A thin film consisting essentially of Zr, N and optionally Ti, at least a portion of the thin film having a non-columnar grain structure.

2. The thin film of claim 1 having a thickness of less than or equal to about 10 nm.

3. The thin film of claim 1 having a thickness, wherein a first portion of the thickness comprises the non-columnar grain structure and wherein a second portion of the thickness comprises columnar grains.

4. The thin film of claim 3 wherein the columnar grains have diameters of from about 10 nm to about 20 nm.

5. The thin film of claim 3 wherein the thin film is disposed over a silicon dioxide surface and wherein the first portion of the thickness is disposed closer to the silicon dioxide surface than is the second portion.

6. The thin film of claim 1 having an atomic ratio of Ti to Zr greater than or equal to 1.0.

7. The thin film of claim 5 consisting essentially of Ti, Zr and N.

8. The thin film of claim 1 wherein the N is present in the thin film at from about 40 atomic percent to about 60 atomic percent.

9. The thin film of claim 1 having a resistivity of from about 69 μΩ·cm to about 106 μΩ·cm.

10. A barrier layer comprising Ti and Zr, a first portion of the barrier layer comprising a non-columnar grain structure, and a second portion of the layer comprising columnar grain structure.

11. The barrier layer of claim 10 further comprising one or more elements selected from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nd, Sc, Sr, Y, Mn, V, Si, Fe, Co, Ni, B, C, La, Pr, P, S, Sm, Gd, Dy, Ho, Er, Yb, W, Cr, Mo, Nb, and Ta.

12. The barrier layer of claim 10 disposed between a metallic material and a non-metallic material.

13. The barrier layer of claim 12 wherein the non-metallic material comprises a member of the group consisting of SiO_2 and low-k dielectric materials.

14. The barrier layer of claim 12 wherein the metallic layer comprises copper.

15. The barrier layer of claim 13 having a thickness of from about 10 nm to about 20 nm, wherein the first portion of the layer is closer to the non-metallic material than is the second portion.

16. A metal diffusion barrier comprising:

a first layer comprising Ti and Q and being substantially nitrogen free, where Q comprises one or more elements selected from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nd, Sc, Sr, Y, Mn, V, Si, Fe, Co, Ni, B, C, La, Pr, P, S, Sm, Gd, Dy, Ho, Er, Yb, W, Zr, Cr, Mo, Nb, and Ta; and

a second layer comprising $(TiQ)_xN_z$.

17. The metal diffusion barrier of claim 16 wherein Q comprises Zr.

18. The metal diffusion barrier of claim 16 wherein the second layer is over the first layer, and further comprising a third layer over the second layer, the third layer comprising Ti and Zr and being essentially free of nitrogen.

19. The metal diffusion barrier of claim 16 wherein the first layer is over the second layer, and further comprising a third layer over the first layer, the third layer comprising $(TiQ)_xN_z$.

20. The metal diffusion barrier of claim 16 disposed between a metallic material and a non-metallic material.

21. A copper diffusion barrier comprising a bi-layer, a first portion of the bi-layer comprising TiZr, and a second portion of the bi-layer comprising $(TiZr)_xN_z$

22. The copper diffusion barrier of claim 21 wherein the second portion comprises non-columnar grain structure.

23. The copper diffusion barrier of claim 21 wherein the second portion is adjacent a layer of silicon dioxide and the first portion is adjacent a copper based material.

24. A titanium-comprising material having an electrical resistivity of from about 69 µΩ•cm to about 106 µΩ•cm, and having a substantially uniform thickness.

25. The titanium-comprising material of claim 24 further comprising Zr.

26. The titanium-comprising material of claim 25 having an atomic ratio of Ti to Zr of greater than or equal to 1, and further comprising from about 40 atomic percent to about 60 atomic percent N.

27. The titanium-comprising material of claim 24 further comprising N.

28. A copper barrier film having a first portion comprising a non-columnar grain structure, and a second portion comprising a columnar grain structure, the film having a substantial absence of amorphous phase material.

29. The film of claim 28 comprising Ti.

30. The film of claim 28 comprising Zr.

31. The film of claim 28 comprising Ti, Zr and N.

32. The film of claim 28 consisting essentially of $(TiZr)_xN_z$, where x = 0.40-0.60 and z = 0.40-0.60.

33. The film of claim 18 having an electrical resistivity of from about 69 µΩ•cm to about 106 µΩ•cm.

34. The film of claim 28 having a thickness of less than 20 nm.

35. A diffusion protected surface comprising:

a material having a surface; and

a thin film consisting essentially of Zr and N and optionally Ti over the surface, at least a portion of the thin film having a non-columnar grain structure.

36. The diffusion protected surface of claim 35 wherein the thin film

AMENDED SHEET (ARTICLE 19)

comprises Ti.

37. The diffusion protected surface of claim 35 wherein the material having the surface comprises a non-metallic material.

38. The diffusion protected surface of claim 35 wherein the material having the surface comprises SiO_2.

39. The diffusion protected surface of claim 35 wherein the thin film is disposed between the surface and a metallic material comprising one or more of Cu, Ag, Sn, Mg and Al.

40. A structure comprising:

a silicon substrate;

a insulative material over the substrate;

a barrier layer consisting essentially of $(TiZr)_xN_z$ over the insulative material, the barrier layer having a substantial absence of amorphous structure, at least a portion of the barrier layer comprising non-columnar grain structure; and

a layer comprising a metal over the barrier layer.

41. The structure of claim 40 wherein x = 0.44-0.60 and z = 0.40-0.60.

42. The structure of claim 40 wherein the metal comprises copper.

43. The structure of claim 40 wherein the metal comprises copper, wherein the insulative material comprises SiO_2; wherein the barrier layer has a thickness of less than or equal to about 5 nm; and wherein, the barrier layer substantially prevents diffusion of copper from the layer comprising the metal into the SiO_2 during heat treatment of the structure at a temperature of about 650°C for about 1 hour.

44. The structure of claim 40 wherein the metal comprises copper, wherein the insulative material comprises SiO_2; wherein the barrier layer has a thickness of less than or equal to about 20 nm; and wherein, the barrier layer substantially prevents diffusion of copper from the layer comprising the metal into the SiO_2 during heat treatment of the structure at a temperature of about 700°C for about 5 hours.

45. A microelectronic device comprising:

a insulative material comprising an opening having a bottom surface and a sidewall surface;

a barrier layer over the bottom surface, the barrier layer comprising Ti and Zr, and having an electrical resistivity of less than or equal to about 69 μΩ•cm to about 106 μΩ•cm; and

a material comprising copper disposed over the barrier layer.

46. The microelectronic device of claim 45 wherein the opening has a width of less than or equal to about 350 nm.

47. The microelectronic device of claim 45 wherein the opening has a width of less than or equal to about 100 nm.

48. The microelectronic device of claim 45 wherein the barrier layer is disposed over the sidewall surface.

49. The microelectronic device of claim 48 wherein the barrier layer has a substantially uniform thickness over the bottom surface and over the sidewall surface.

50. The microelectronic device of claim 49 wherein the opening has a height to width aspect ratio of greater than or equal to 1.

51. The microelectronic device of claim 50 wherein the aspect ratio is greater than 2.

52. The microelectronic devise of claim 49 wherein thickness is less than or equal to about 20 nm.

53. The microelectronic devise of claim 49 wherein thickness is less than or equal to about 5 nm.

54. The microelectronic devise of claim 45 wherein the barrier layer comprises an atomic ratio of Ti to Zr of greater than or equal to 1.0.

55. The microelectronic devise of claim 45 wherein the barrier layer further comprises N.

56. The microelectronic device of claim 55 wherein the barrier layer

comprises from about 40 atomic percent to about 60 atomic percent N.

57. The microelectronic device of claim 55 wherein the barrier layer consists essentially of Ti, Zr and N.

58. The microelectronic device of claim 55 wherein the barrier layer consists of Ti, Zr, and N.

59. The microelectronic device of claim 45 wherein the material comprising copper consists essentially of copper.

60. A method of forming a barrier layer comprising:

providing a substrate comprising a material to be protected;

providing a target comprising Ti and Zr; and

in the presence of an Ar/N_2 plasma, ablating material from the target onto the substrate at a deposition power of from about 2 kW to about 9 kW, the ablating forming a barrier layer comprising Ti, Zr and N and having a substantially uniform thickness over at least a portion of the material to be protected.

61. The method of claim 60 wherein the target consists essentially of Ti and Zr.

62. The method of claim 60 wherein the barrier layer has an atomic ratio of Ti to Zr of greater than or equal to about 1.

63. The method of claim 60 wherein the barrier layer has an electrical resistivity of from about 69 μΩ•cm to about 106 μΩ•cm.

64. The method of claim 60 further comprising depositing a conductive material over the barrier layer, the conductive material comprising a metal.

65. A method of forming a microelectronic device, comprising:

providing a substrate having one or more gap structures formed in an insulative material;

lining the gap structures with a layer comprising Ti, the layer having a substantially uniform thickness and having an electrical resistivity of from about 69 μΩ•cm to about 106 μΩ•cm;

depositing a copper material over the layer.

66. The method of claim 65 wherein the layer further comprises N and one or more elements selected from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nd, Sc, Sr, Y, Mn, V, Si, Fe, Co, Ni, B, C, La, Pr, P, S, Sm, Gd, Dy, Zr, Ho, Er, Yb, W, Cr, Mo, Nb, and Ta.

67. The method of claim 66 wherein the layer consists essentially of Ti, Zr and N.

68. The method of claim 65 wherein the one or more gap structures comprise openings having a height to width aspect ratio of greater than or equal to 4.

69. The method of claim 68 wherein the openings have a width of less than or equal to about 350 nm.

70. The method of claim 68 wherein the openings have a width of less than or equal to about 200 nm.

71. The method of claim 68 wherein the openings have a width of less than or equal to about 100 nm.

72. The method of claim 65 wherein the insulative material comprises SiO_2.

73. A method of forming a protected surface comprising:

providing a substrate having a surface into a reaction chamber;

providing a target within the reaction chamber, the target consisting essentially of Ti and Zr;

ablating material from the target onto the surface in the presence of nitrogen to deposit a first layer over the surface; and

ablating material from the target in an absence of added nitrogen to form a second layer over the first layer.

74. The method of claim 73 wherein the surface comprises silicon dioxide.

75. The method of claim 73 wherein the first layer has a thickness of less than or equal to about 10 nm, and has a microstructure consisting essentially of non-columnar grains.

76. The method of claim 73 wherein the first layer has a thickness of greater than about 10 nm, and comprises a first portion having non-columnar grain structure and a second portion comprising columnar grain structure.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01L 23/48; H01L 21/44
US CL :257/4, 751, 761, 764; 438/17, 592, 643, 653, 656, 685
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 257/4, 751, 761, 764; 438/17, 592, 643, 653, 656, 685

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 6,204,171 B1 (HU) 20 March 2001, col. 6, line 42 to col. 10, line 57.	1, 9, 11-12, 36-39, 41-43 --------- 2-8, 10, 13-16, 40, 44, 63-65
X -- Y	US 6,156,647 A (HOGAN) 05 December 2000, col. 9, line 20 to col. 10, line 27.	62, 66 --------- 2-8, 13-16, 40, 44, 63-64
Y	WOLF, Silicon Processing for the VLSI Era, vol. 2, pages 189-190, Table 4.3 on page 193.	10, 65

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,329,275 B1 (Ishigami et al.) 11 December 2001, col. 4, line 52 to col. 5, lin 28.	1, 9, 11-15, 17-35, 41-44